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Synthesis, Complexation and Photophysics of *1,3-alternate* Calix[4]arene-crowns-6 Bearing Fluorophoric Units on the Bridge

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Three new calix[4]arene-crown-6 derivatives bearing a fluorophoric unit on the ether bridge were synthesized. All these compounds complex alkali metal picrates in chloroform, and the naphthocrown (2) shows the highest efficiency for cesium ion binding among the calix-crown-6 known so far. Cesium over sodium selectivity is remarkably higher in acetonitrile than in chloroform solution. ^{1}H NMR studies, carried out in $CDCl_3$ on the cesium picrate complex of ligand 2, show that the anion is involved in a $\pi-\pi$ stacking with the naphthyl unit. The lariat calix[4]-crown-6 (4) does not show any relevant change in absorption and fluorescence spectra upon cesium binding, thus indicating that the dansyl unit is not perturbed by metal ion complexation. On the contrary, for ligands 2 and 3 a luminescence intensity decrease is observed upon cation binding, which allows an easy detection of cesium even at very low concentrations (10^{-7} M).

Keywords: Calix[4]arene-crown-6; Cesium; Alkali metal ions; Photophysics; Luminescence; Fluorescence

INTRODUCTION

Calix[4]arene-based ligands have been widely used in the last years in spherical metal ions and especially in alkali metal ions recognition [1]. Among these ligands, calix[4]arene-crown-n (n = 4–6) ethers (calix[4]crowns) [2], present the highest selectivity for sodium, potassium or cesium, respectively. They have been used for the alkali metal ions separation through supported liquid membranes (SLMs') [3–6], or in detection using potentiometric sensors such as ion-selective electrodes (ISEs') or ion-selective field effect transistors (ISFETs') [4,7]. More recently, calix[4]crowns have been modified by introducing chromophores or fluorophores at the upper or lower rim of the calix, in order to obtain an optical transduction of the

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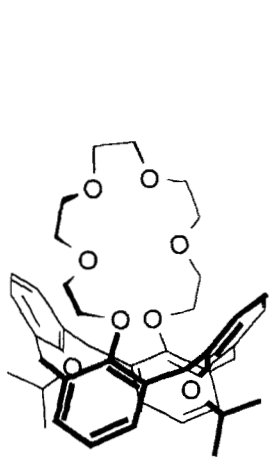
complexation event [8, 9]. Photoluminescence spectroscopy offers several advantages in terms of sensitivity and versatility, and can find application in several fields allowing the monitoring of analyte concentration in real-time and real-space [9–12].

Calix[4]crowns-4 were modified by Shinkai *et al.* by introducing phenyl or pyrene substituents at the upper rim [13, 14]. These derivatives show a more than 5 times increase in the fluorescence upon sodium or lithium (but not potassium) binding. Dabestani *et al.* synthesised a calix[4]arene-biscrown-6 and a calix[4]arene-diaza-crown-6 bearing anthracene units appended on the ether bridge, which are able to optically detect cesium [15, 16]. The emission of the free ligands is quenched through a photoinduced electron transfer (PET), and cesium complexation causes an increase of this property. However, in the calix[4]arene-diaza-crown-6, the presence



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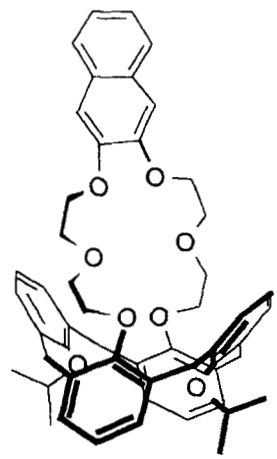

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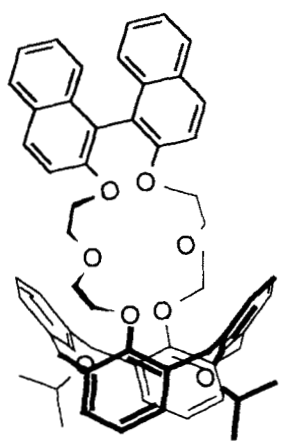

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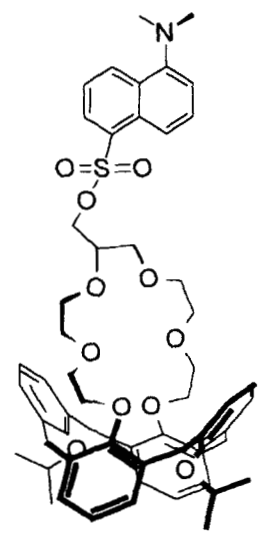

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FORMULAS 1–4

of two nitrogen instead of oxygen atoms induces a significant decrease of the binding constant (K_{ass}) for cesium compared to that of di-*iso*-propoxycalix[4]arene-crown-6 (**1**) [16]. This indicates once again that synthetic modifications aiming at introducing efficient fluorophores on a calixarene-based ionophore, may result in a remarkable change in the binding properties. Very recently we showed that also the calixarene chromophore of calix[4]crowns blocked in the *1,3-alternate* conformation (*e.g.*, **1**) undergoes monitorable and sometimes pronounced changes in the fluorescence intensity upon alkali or silver ion complexation, thus suggesting that cation $-\pi$ interactions may play an important role in tuning the luminescence properties of these hosts [17]. It is also known that calix[4]arenebenzo-crown-6 [6, 18, 19] and benzo-biscrown-6 [20–22] ethers show an improved cesium/sodium selectivity with respect to calix[4]crown-6 (**1**), as a consequence of both an increase of cesium and a decrease of sodium binding. This seems to be due to several factors, such as a higher rigidification, complementarity and hydrophobicity of the benzocrown loop [21]. On these bases and in order to increase the luminescence of the hosts, but keeping the binding groups as close as possible to the ideal disposition of calix[4]arene-crown-6 in *1,3-alternate* conformation, we have synthesised two new calix[4]arene-crown-6 **2** and **3** having a 2,3-naphthalene or a 2,2′-binaphthyl fluorophore in the crown bridge. In addition we also synthesised a *lariat* calix[4]crown [23] ether **4** which presents a dansyl group appended on a side-arm of the crown moiety.

RESULTS AND DISCUSSION

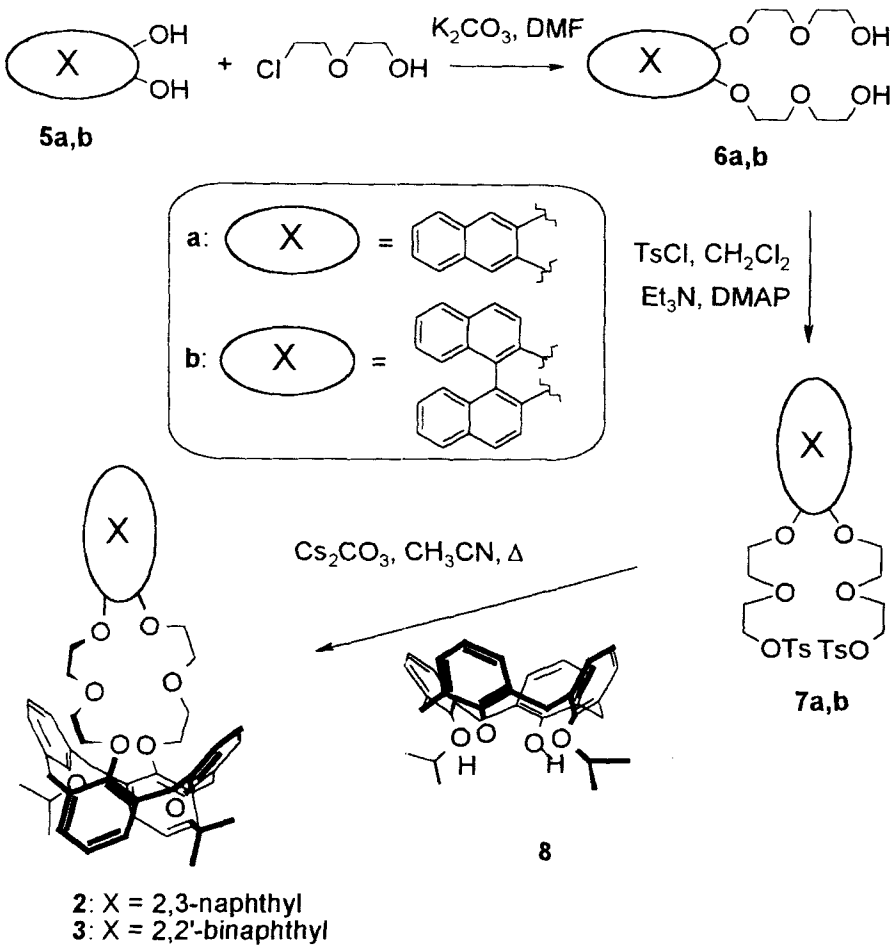
Synthesis of Oligoethylene Glycols

The synthesis of calix[4]crowns **2** and **3** bearing fluorophoric groups (naphthalene or binaphthyl) in the oligoethylene chain requires the preparation of ditosylates **7a,b** (Scheme 1). Although the synthesis of **7a** [24] and **7b** [25] was already reported in the literature, it requires the protection of one end of diethylene glycols with tetrahydropyranosyl or benzyl groups and deprotection after coupling with the aromatic unit. More convenient is the use of the commercially available 2-chloroethoxy ethanol. By heating for 30–48 hs a solution of 2,3-dihydroxynaphthalene or (±) 2,2′-binaphthol with a ten-fold excess of K_2CO_3 and 2-chloroethoxy ethanol, the glycols **6a** and **6b** can be isolated in 68 and 58% yield, respectively. Subsequent reactions of glycols **6a,b** with tosyl chloride, triethylamine and a catalytic amount of dimethylamino pyridine (DMAP) give ditoylates **7a,b** in excellent yields.

For the synthesis of the lariat calix[4]crown **4** the glycol **12** bearing a protected side-arm was needed. We have recently shown that 2-allyloxy glycerol **10** is a useful synthon for the preparation of lariat crowns [23]. Glycerol **10**, can be used in its enantiomerically pure (R) isomer derived from mannitol, or as racemic mixture which is commercially available at low price. Reaction of glycerol **10** with monotrityl monotosyl diethylene glycol **9** [23] and NaH in DMF (Scheme 2) gives dialkylated compounds **11** in 34% yield after column chromatography. The low yield of **11** should be mainly ascribed to a low reactivity of the secondary hydroxyl groups of glycerol **10** which results in the formation of a large amount of monoalkylated glycerol. Removal of trityl groups followed by reaction of the resulting diol **12** with tosyl chloride gives ditosylate **13** in 86%.

Synthesis and Conformational Properties of Calix[4]crowns 2–4

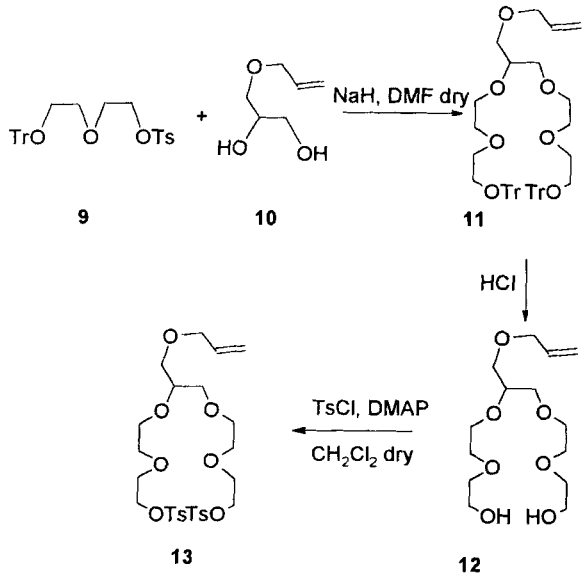
Calix[4]crowns **2** and **3** are isolated in >90% yields by using the appropriate tosylate (**7a** and **7b**) and the well-known conditions (Cs_2CO_3 as base in refluxing acetonitrile) for the obtainment of *1,3-alternate* conformers (Scheme 1) [3, 26]. The stereochemical outcome of the reaction was



SCHEME 1

evaluated by ^{1}H and ^{13}C NMR, which confirm that calix[4]crowns **2** and **3** are blocked in the *1,3-alternate* conformation [27]. For compound **2** two distorted doublets in the ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) at 3.78 and 3.73 ppm and a triplet at 38.6 ppm in the ^{13}C spectrum are present. More complicated are the spectra of the binaphthylcalix[4]crown **3** since the presence of the chiral unit generates a C_2 symmetry axis only. The methylene bridge $ArCH_2Ar$ protons of **3** are therefore splitted into two doublets (AB system: $\delta_H = 3.67$ and 3.80, $J = 15.3$ Hz) and a singlet ($\delta_H = 3.79$) while the corresponding carbons give two triplets at $\delta_C = 38.6$ and 38.7.

The allyl protected lariat calix[4]crown-6 (**14**) was obtained in 88% yield, comparable to that of compounds **2**–**3**. The allyl group was removed with *p*-toluenesulfonic acid (PTSA) and Pd/C in ethanol/dichloromethane and the lariat alcohol **15** was obtained in 60% yield (Scheme 3). The alcohol **15** is a useful intermediate for the synthesis of lariat calix[4]crowns-6 bearing additional binding groups or chromophoric units in the side arm. We chose to introduce a dansyl group since this is well-known for its fluorescence properties. By reacting dansyl chloride, triethylamine and DMAP in dry CH_2Cl_2 the dansyl derivative **4** was isolated

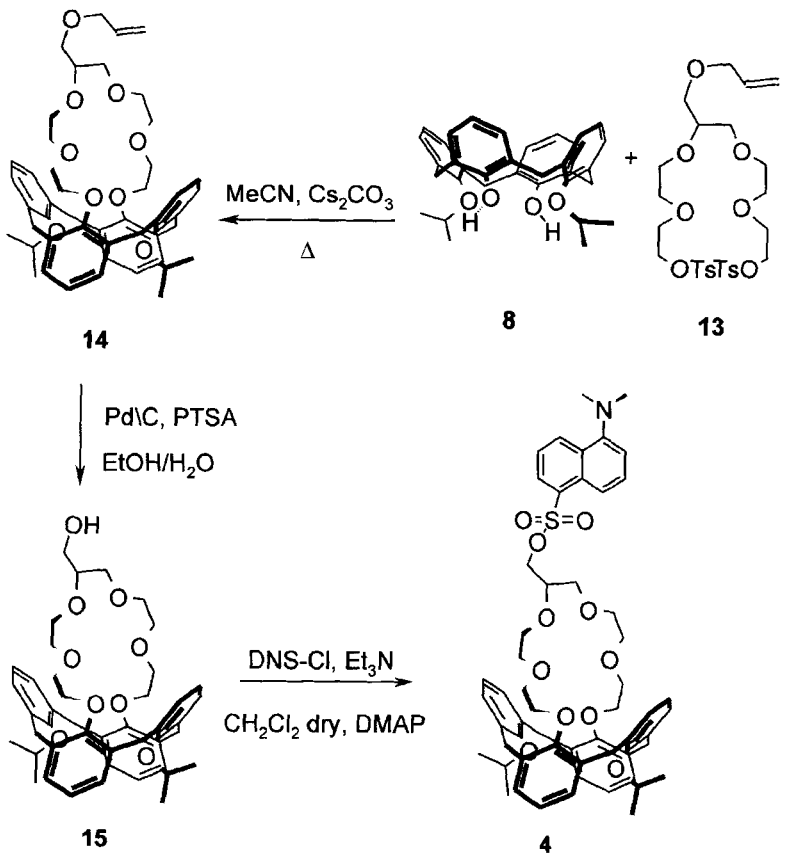


SCHEME 2

pure in 50% yield after preparative layer chromatography.

Complexation Properties

All ^1H NMR spectra of the complexes obtained by stirring for 24 hs a $CDCl_3$ solution of calix[4]crowns **2**–**4** with 3 equivalents of solid cesium picrate (CsPic) show the presence of the singlet of the picrate anion at low fields. The integration of the signals indicates the formation of the 1:1 complex in all cases. Moreover, the signals of the oxyethylene protons of the crown moieties are downfield shifted with respect to the corresponding protons in the free ligand, indicating they are interacting with the cesium ion. While for the protons of the naphthalene units of binaphtyl- (**3**) and dansyl calix[4]crown



SCHEME 3

(4) there are only minor shifts upon cesium complexation, unexpected upfield shifts are observed in naphthocalix[4]crown **2**. All the protons of the naphthalene unit absorb at lower frequencies ($\Delta\delta_{H1,4} = -0.30$, $\Delta\delta_{H5,8} = -0.15$, $\Delta\delta_{H6,7} = -0.10$). Also the signal of the protons of the picrate anion is found at 8.48 ppm (Fig. 1), largely displaced from the 8.8 ppm position where it is usually present in the spectra of calix[4]crowns-6 cesium complexes [3]. These data seem to indicate that in $CDCl_3$ the picrate is stacking on the naphthyl unit of **2**.

We have evaluated association constants of ligands **2**–**4** in $CDCl_3$ using the Cram's method [28, 29] and the values obtained are reported in Table I and compared with those of 1,3-di-*iso*-propoxycalixcrown-6 (**1**) [3]. From these data it clearly emerges that naphthocrown **2** gives a more efficient complexation of cesium cation than calix[4]crowns **3** and **4** and even **1**. The efficiency in cesium binding follows the order **2** > **1** > **4** > **3**.

The behavior of naphthocalix[4]crown **2** slightly contrasts with what we previously observed [18] with calixbenzocrowns and others [21] with calixbis(benzocrowns). The association constants of aromatic crown ethers with alkali metal ions are usually lower compared with aliphatic counterparts having the same ring size [30]. For ligand **2** in chloroform it is likely, as shown by ^1H NMR spectroscopy, that a stabilising $\pi-\pi$ stacking interaction between the picrate and the naphthyl unit is occurring. Since with naphthocrown **2** also all the other alkali cations are better extracted than with **1**, it results that **2** has a slightly lower selectivity than **1**. In particular, cesium over sodium selectivity which is technologically important for decategorisation of radioactive waste, is slightly lower for **2** ($\Delta\Delta G^\circ = 16.4$ kJ/mol) than for **1**

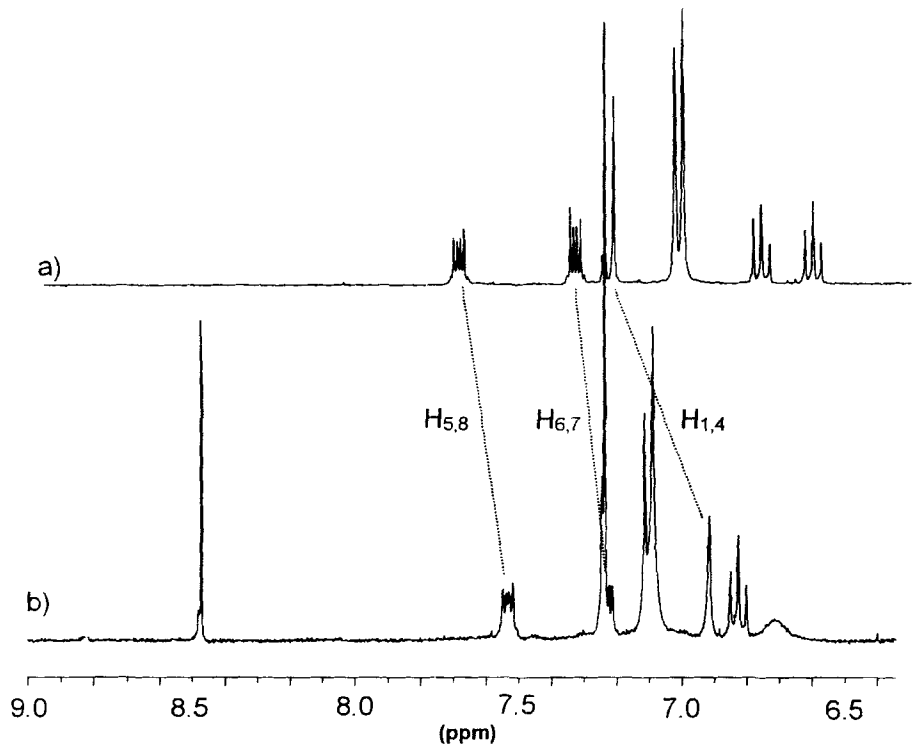


FIGURE 1 Portion of the ^1H NMR spectrum ($CDCl_3$, 300 MHz) of (a) ligand **2** and (b) its cesium picrate complex.

TABLE I Association constants (Ka)* and binding free energies ($-\Delta G°$, kJ/mol) of complexes of calixcrowns-6 with alkali metal picrates in $CHCl_3$ saturated with water at 22°C

	Log K_a				$-\Delta G°$			
Ligand	Na^+	K^+	Rb^+	Cs^+	Na^+	K^+	Rb^+	Cs^+
2	6.5	7.3	8.4	9.4	36.7	41.2	47.4	53.1
3	< 5	< 5	6.7	7.2	< 28	< 28	37.8	40.7
4	7.6	7.7	7.9	8.5	42.9	43.5	44.6	48.0
1	5.2	6.4	7.9	8.8	29.2	36.8	44.6	49.4

* *error* < 10%.

($\Delta\Delta G° = 20.2$ kJ/mol). The binaphthocrown **3** is the least efficient calix[4]crown in the series herein prepared, probably because of the larger size (closer to a calix[4]crown-7 than to a calix[4]crown-6) and to the distortion induced by the binaphtyl unit. Lariat calix[4]crown **4** is quite efficient in the complexation of all alkali metal ions, but its selectivity for cesium is modest.

We have also determined association constants in acetonitrile by spectrophotometric and spectrofluorimetric titrations [31]. The data are reported in Table II with the exception of those for ligand **4** since no significant changes were observed in its absorption spectra (*vide infra*) upon addition of alkali metal salts.

Interestingly, ligand **2** shows for cesium one of the highest association constants known so far in the family of calix[4]crowns or calix-biscrowns. It shows a LogKa of 0.5 log units higher than that of calix[4]arene-bis(naphthocrown-6) [32] although still lower than that of calix[4]arene-bis(dibenzocrown-6) [21]. Sodium is not significantly bound in acetonitrile, thus resulting in a remarkable cesium/sodium selectivity ($\Delta\Delta G° > 24.8$ kJ/mol).

Photophysical Properties of the Hosts and of Their Metal Complexes

Absorption Spectra

The absorption band of the calix[4]-crown **1** is, as previously reported, centred at 270 nm, with an absorption coefficient of 1550 $M^{-1}cm^{-1}$. In hosts **2–4** the chromophore is inserted in the structure of the calix-crown skeleton to improve the capability of the host molecule to signal the metal ion complexation process. The chosen chromophores present much higher absorption coefficients and their absorption bands are more red-shifted compared to the calix[4]crown **1**. As a consequence, the absorption spectra of the hosts (Fig. 2) are in all cases dominated by the absorption bands of the appended chromophore, being the absorption due to the calixarene aromatic rings almost negligible.

For host **2**, the absorption band due to the 2,3-dimethoxynaphthalene chromophore in the 270–330 nm region has been already assigned [33] to a $\pi-\pi^*$ transition. Addition of alkali metal ions to a solution of **2** slightly modifies the spectrum, leading to an intensity decrease (22%

TABLE II Association constants (Ka)* and binding free energies ($-\Delta G°$, kJ/mol) of complexes of calixcrowns-6 with alkali metal perchlorates in acetonitrile at 25°C

	LogKa				$-\Delta G°$			
Ligand	Na^+	K^+	Rb^+	Cs^+	Na^+	K^+	Rb^+	Cs^+
2	< 1.0	4.2	5.3	5.4	< 6	23.9	30.2	30.8
3	< 1.0	3.4	4.3	4.5	< 6	19.4	24.5	25.7

* *errors* < 10%; *nd* = *not determined*.

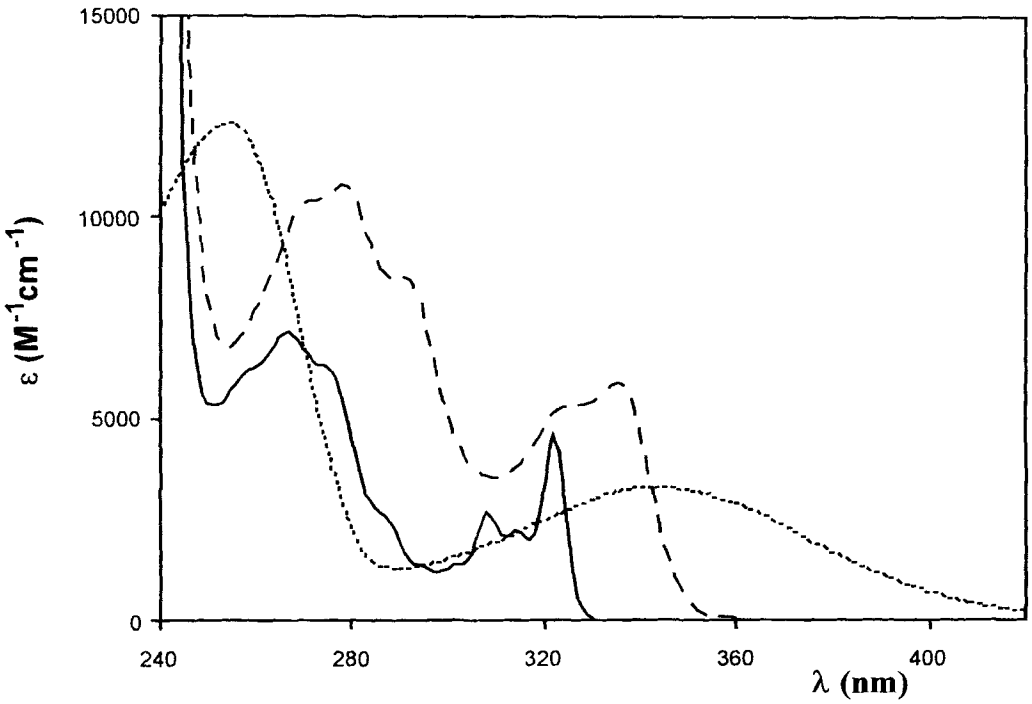


FIGURE 2 Absorption spectra of hosts **2** (_____), **3** (– – – – –), and **4** (.....) in acetonitrile solutions at room temperature.

in the case of Cs^+) and to a small blue shift (2 nm) of the absorption bands in the 300–330 nm region. This effect can be attributed to the interaction of the metal cation with the oxygen atoms directly linked to the chromophore, influencing in this way their conjugative effect to the π-system of the naphthalene. The intensity decrease is stronger on going from K^+ to Cs^+.

The absorption spectrum of **3** is dominated by the bands due to $\pi-\pi^*$ transitions of the binaphthyl moiety [34,35]. In this case, complexation with alkali metal ions (see Fig. 3 for Cs^+) leads to much stronger changes in the absorption bands of the chromophore with respect to those observed for host **2**. For **3**, complexation not only decreases the resonance of the oxygens lone pairs with the aromatic nuclei, but induces also a distortion of the angle between the two naphthalene rings, reducing in this way their conjugation and, as a consequence, the molar absorption coefficient of the system. In this contest, the larger Cs^+ ion is expected to create the largest distortion, and therefore the largest effect on the absorption spectrum, as indeed observed.

Host **4**, containing the dansyl chromophore, shows an absorption band with maximum at 340 nm, corresponding to a charge transfer transition from the lone-pair on the amino group into a π antibonding orbital of the naphthalene ring of the chromophore [36]. No relevant changes were observed for this host upon metal ion complexation. This indicates that the electronic density of chromophore is substantially not perturbed by metal ion complexation in the crown cavity, suggesting that its sulfonato group is not coordinated to the cation.

Fluorescence Spectra

The fluorescence spectra of host **1** shows a band with maximum at 311 nm, previously assigned to a $\pi-\pi^*$ transition occurring in the aromatic

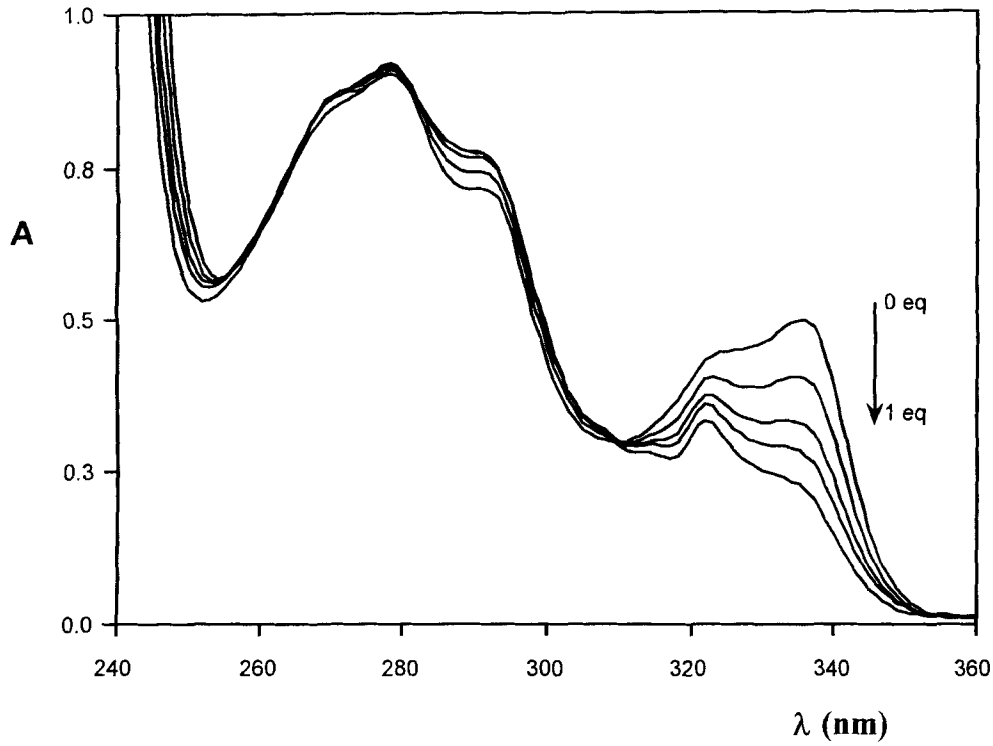


FIGURE 3 Changes on the absorption spectra of an acetonitrile solution of host **3** upon addition of increasing amounts of $CsClO_4$.

TABLE III Photophysical properties of the hosts **2–3** and of their metal ion complexes in acetonitrile solutions at 25°C

Compound	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)	λ_{max} (nm)	Φ	τ (ns)
2	268	7100	341	0.41	9.2
	323	4600			
2.Na^+	268	7050	341	0.39	9.1
	322	4250			
2.K^+	268	7000	341	0.38	8.9
	322	3900			
2.Rb^+	268	6950	340	0.37	8.4
	321	3730			
2.Cs^+	268	7000	340	0.36	8.2
	321	3620			
3	279	10700	367	0.52	5.5
	336	5900			
3.K^+	279	10700	366	0.51	5.4
	336	3500			
3.Rb^+	279	10600	366	0.49	5.3
	334 (s)	2200			
3.Cs^+	279	10550	366	0.46	4.9
	333 (s)	2020			
4	255	13000	540	0.44	11.9
	340	3280			

rings of the calixarenes. This band can not be observed in the spectra of the hosts **2**–**4** (Fig. 4).

In principle, energy transfer from this state to the lowest excited state of the chromophore is possible for all the hosts; it is however almost impossible to prove it, due to the negligible absorption of the aromatic rings of the calixarene skeleton compared to the absorption of the appended chromophore. Fluorescence spectra are thus dominated by transitions arising from the lowest energy singlet excited state of the appended chromophore, the same responsible of the absorption bands discussed above. For hosts **2** ($\lambda_{max} = 341$ nm, $\tau = 9.2$ ns) and **3** ($\lambda_{max} = 367$ nm, $\tau = 5.5$ ns), these transitions are of a $\pi-\pi^*$ type, while for host **4** ($\lambda_{max} = 539$ nm, $\tau = 11.9$ ns) fluorescence is originated from the above discussed charge transfer state. The fluorescence of the latter host does not change upon metal ion complexation, again indicating that the dansyl chromophore is too far away for 'sensing' the association event. On the contrary, a decrease in the fluorescence intensity and excited state lifetime was observed when metal ions were added to a solution of **2** or **3** (see Fig. 5), that can be attributed to the reasons discussed for the absorption spectra.

For both hosts **2** and **3**, the largest changes can be monitored in the absorption and fluorescence spectra upon addition of Cs^+. This finding, together with the data obtained from binding experiments, leads to the interesting conclusions that these hosts selectively bind and selectively respond to Cs^+ over the other alkali metal ions. In addition, since the observed intensity is proportional, when working in dilute conditions, both to the fluorescence quantum yield and to the molar absorption coefficient at the excitation wavelength [37], the observed decreases in absorption and luminescence intensities combine in a synergic way in amplifying the signal changes upon complexation. As a result, upon excitation at 335 nm, an intensity decrease up to 70% can be monitored

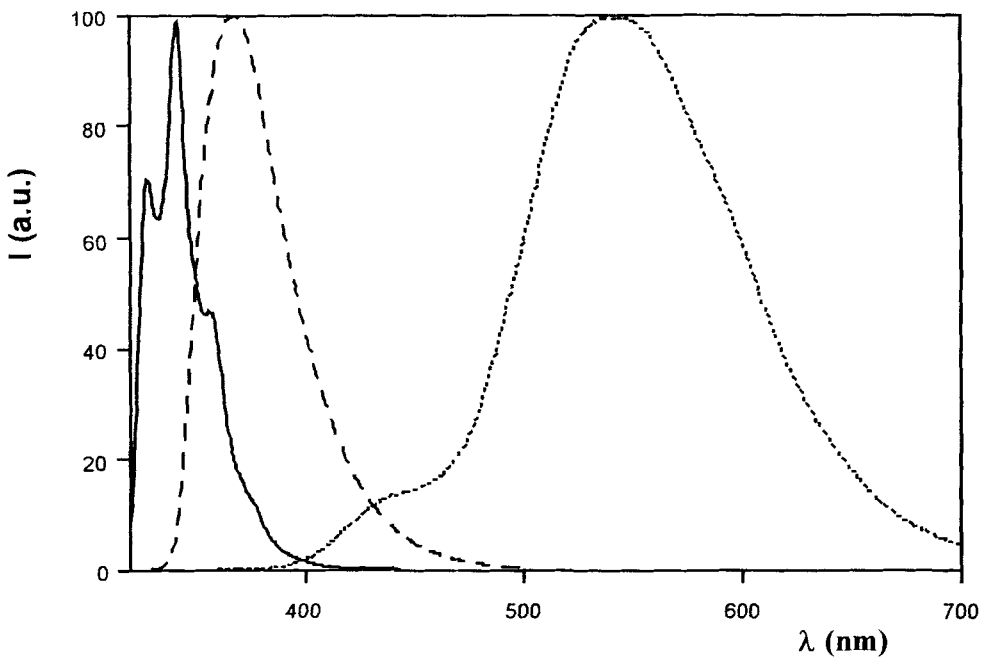


FIGURE 4 Fluorescence spectra of hosts **2** (_____, $\lambda_{exc} = 295$ nm), **3** (– – – – –, $\lambda_{exc} = 269$ nm), and **4** (. . . . . , $\lambda_{exc} = 340$ nm) in acetonitrile solutions at room temperature.

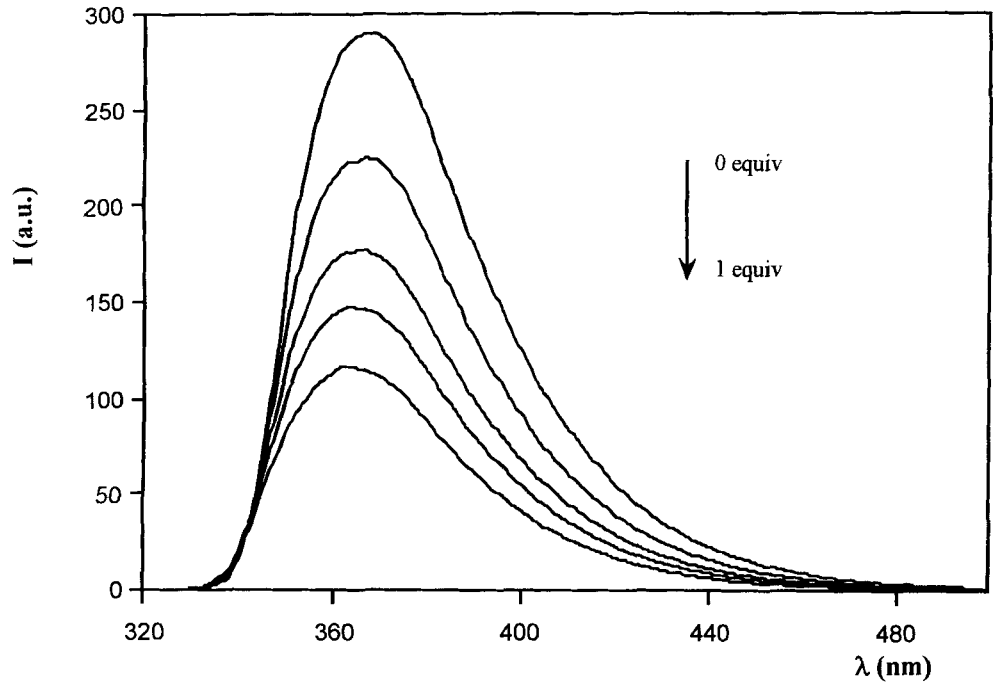


FIGURE 5 Changes on the fluorescence spectra ($\lambda_{exc} = 335$ nm) of an acetonitrile solution of host **3** upon addition of increasing amounts of $CsClO_4$.

upon addition of 1 equivalent of Cs^+, a decrease that allows an easy detection of Cs^+ concentration even in very dilute (10^{-7}M) conditions.

Experimental Section

Melting points were determined with an Electrothermal melting point apparatus in a sealed capillary. ^1H and ^{13}C NMR spectra were recorded with a Bruker AMX400 (^1H:400 MHz), AC300 (^1H:300 MHz, ^{13}C:75 MHz) spectrometers of the Centro Interdipartimentale di Misure (C.I.M.) of the University of Parma using Me_4Si as internal standard. Mass spectra were obtained with a Finnigan MAT SSQ710 spectrometer (DCI using methane as ionizing gas). CH_3CN was dried over molecular sieves (3Å). Analytical TLC were performed on precoated silica gel plates (SiO_2, Merck, 60 F_{254}), while silica gel 60 (SiO_2, Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for preparative flash column chromatography. 25,27-bis(2-propyloxy)calix[4]arene (**8**) [38] and monotrityl monotosyl diethyleneglycol (**9**) [23] were prepared as described in literature.

For spectrophotometric measurements acetonitrile Uvasol (Merck) was used as a solvent. Solutions of hosts were 5.0×10^{-5}M unless otherwise noted. Absorption spectra were recorded with a Perkin Elmer lambda 40 spectrophotometer. Uncorrected emission, and corrected excitation spectra were obtained with a Perkin Elmer LS 50 spectrofluorimeter. The fluorescence lifetimes (uncertainty ±5%) were obtained with an Edinburgh single-photon counting apparatus, in which the flash lamp was filled with D_2. Luminescence quantum yields (uncertainty ±15%) were determined using quinine sulphate in 1N H_2SO_4 aqueous solution ($\Phi = 0.546$) [39] as a reference. In order to allow comparison among emission intensities, we performed corrections for instrumental response, inner filter effects, and phototube

sensitivity [37]. A correction for differences in the refraction index was introduced when necessary. Determination of association constants in CH_3CN was performed as previously reported [31].

2-(2-(3-[2-(2-Hydroxy-ethoxy)-ethoxy]-naphthalen-2-yloxy)-ethoxy)-ethanol (6a) [24]

To a stirred solution of 2,3-dihydroxynaphthalene **5a** (3.05 g, 0.019 mol) in DMF (110 ml) under nitrogen atmosphere, K_2CO_3 (26.3 g, 0.19 mol) was added and the mixture refluxed for 2 h. Then chloroethoxy ethanol (5.9 ml, 0.056 mol) was slowly dropped and heating continued for 30 h. DMF was removed under reduced pressure, the residue quenched with 1N HCl (100 ml) and CH_2Cl_2 (50 ml) added. The organic layer was separated and washed twice with water (2 × 50 ml) and dried over Na_2SO_4. After removal of the solvent, the reddish oil was chromatographied (SiO_2 : CH_2Cl_2 : MeOH = 9 : 1) and pure compound **6a** obtained.

Yield: 68%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.64 (dd, 2H, J = 6.1 Hz, J = 3.3 Hz, ArH); 7.32 (dd, 2H, J = 3.3, J = 6.1 Hz, ArH); 7.08 (s, 2H, ArH); 4.20–4.17 (m, 4H, $ArOCH_2$); 3.92–3.90 (m, 4H, $ArOCH_2CH_2O$); 3.74–3.72 (m, 4H, OCH_2CH_2OH); 3.67–3.65 (m, 4H, CH_2OH). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 148.3 (s, ArO); 128.7 (s, Ar); 126.1 (d, Ar); 124.0 (d, Ar); 107.6 (d, Ar); 72.4 (t, $ArOCH_2$); 68.8, 67.9 (t, CH_2OCH_2); 61.3 (t, CH_2OH). MS (CI) *m/z*: 336.4 (M^+) 100%.

2-(2-2′-[2-(2-Hydroxy-ethoxy)-ethoxy]-[1,1′]binaphthalen-2-yloxy)-ethoxy)-ethanol (6b) [25]

Compound **6b** was prepared as described for the diol **6a** and using (±)1-1′-bi-2-naphthol **5b** (3.0 g, 0.0105 mol), K_2CO_3 (14.5 g, 0.105 mol) and chloroethoxyethanol (3.32 ml, 0.0315 mol). The reaction mixture was heated for 48h. Pure product **6b** was obtained by column chromatography (SiO_2 : CH_2Cl_2 : MeOH = 12 : 1).

Yield: 58%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.96–7.85 (d, 4H, ArH, J = 9.0 Hz); 7.44–7.12 (m, 8H, ArH); 4.14–3.98 (m, 4H, $ArOCH_2$); 3.49–3.37 (m, 8H, $ArOCH_2CH_2OCH_2CH_2OH$); 3.20–3.16 (m, 4H, CH_2OH). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 154.2 (s, ArO); 134.0 (s, Ar-Ar); 134.1 (s, Ar); 129.4 (s, Ar); 127.8, 126.2, 125.3, 123.7, 120.2, 115.9 (d, Ar); 72.3 (t, $ArOCH_2$); 69.8, 69.5 (t, CH_2OCH_2); 61.5 (t, CH_2OH). MS (CI) *m/z*: 462 (M^+) 100%.

Di-p-toluensulfonate of 2-(2-(3-[2-(2-hydroxy-ethoxy)-ethoxy]-naphthalen-2-yloxy)-ethoxy) (7a)

To a stirred solution of compound **6a** (3.70 g, 10 mmol) in dry CH_2Cl_2 (40 ml) was added triethylamine (6.1 ml, 44 mmol) and a catalytical amount of 4-dimethylamino pyridine (DMAP). After cooling to 0°C, a solution of tosyl chloride (4.18 g, 22.0 mmol) in CH_2Cl_2 (40 ml) was slowly added. The reaction mixture was stirred at room temperature for 14h, quenched with 1N HCl (30 ml) and the organic layer separated and washed twice with water (2 × 30 ml). After the removal of dichloromethane, the reddish oily residue was submitted to column chromatography (SiO_2 : Et_2O) to give pure compound **7a** as a yellowish solid.

Yield: 88%. M.p.: 84–86°C; ^{1}H NMR ($CDCl_3$ 300 MHz) δ (ppm): 7.91 (d, 4H, J = 8.3 Hz, ArH); 7.81 (dd, 2H, J = 6.1 Hz, J = 3.3 Hz, ArH); 7.47 (dd, 2H, J = 6.1 Hz, J = 3.3 Hz, ArH); 7.39 (d, 4H, J = 8.3 Hz, ArH); 7.25 (s, 2H, ArH); 4.33 (t, 4H, J = 4.8 Hz, $ArOCH_2$); 4.30 (t, 4H, J = 4.7 Hz, CH_2OTs); 4.00 (t, 4H, J = 4.8 Hz, $ArOCH_2CH_2O$); 3.94 (t, 4H, J = 4.7 Hz, OCH_2CH_2OTs); 2.50 (s, 6H, $ArCH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 148.9 (s, ArO); 144.6 (s, $ArOSO_2$); 129.7 (s, $ArCH_3$); 129.3, 127.8 (d, Ar); 127.9 (s, Ar); 126.3 (d, Ar); 108.5 (d, Ar); 69.6, 69.3, 68.9, 68.4 (t, $ArOCH_2CH_2OCH_2CH_2OTs$); 21.5 (q, $ArCH_3$). MS (CI) *m/z*: 644 (M^+).

Di-p-toluensulfonate of 2-(2-2'-[2-(2-hydroxy-ethoxy)-ethoxy]-[1,1']binaphthalen-2-yloxy)-ethoxy) (7b) [40]

Ditosylate **7b** was obtained as described for compound **7a**, using diol **6b**. Column chromatography (SiO_2: ethyl acetate:hexane = 1:1).

Yield: 80%. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.91, 7.80 (d, 4H, ArH, J = 9.0 Hz); 7.70 (dd, 4H, ArH tosyl, J = 9 Hz, J = 1.5 Hz); 7.36–7.10 (m, 12H, ArH tosyl and ArH); 3.98 (m, 4H, $ArOCH_2$); 6.65 (t, 4H, CH_2OSO_2, J = 4.8 Hz); 3.37 (t, 4H, $ArOCH_2CH_2O$, J = 4.8 Hz); 2.95 (m, 4H, $OCH_2CH_2OSO_2$); 2.42 (s, 6H, $ArCH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 154.2 (s, ArO); 144.7 (s, $ArOSO_2$); 133.0 (s, $ArCH_3$); 134.0 (s, Ar-Ar); 129.8 (d, Ar); 127.9 (d, Ar); 127.8, 126.3, 125.3, 123.7, 120.2, 115.3 (d, Ar); 72.3 (t, $ArOCH_2$); 69.8, 69.5, 68.4 (t, $ArOCH_2CH_2OCH_2CH_2O$); 21.5 (q, $ArCH_3$). MS (CI) *m/z*: 770 (M^+) 100%.

1,14-Trityloxy-3,6,9,12-tetroxy-7-allyloxymethyl-tetradecane (11)

A sample of (±) 3-allyloxy-1,2-propandiol **10** (0.58 g, 4.42 mmol) was dissolved in dry DMF (15 ml), the solution was cooled to 0°C, NaH (0.23 g, 9.73 mmol, 50% dispersion on silicon oil) added and the temperature raised to 40°C. After 1h, compound **9** (4.46 g, 8.85 mmol) was added and the reaction mixture heated at 60°C for 12 h. DMF was removed under reduced pressure and the reside quenched (CAUTION!) with water (50 ml) and CH_2Cl_2 (50 ml). The organic layer was separated, washed with water (2 × 50 ml) and dried over Na_2SO_4. Then the solvent was removed at the rotavapor, and the residue submitted to column chromatography (SiO_2: *n*-hexane : Et_2O = 1 : 1).

Yield: 34%. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.56 (m, 6H, ArH); 7.32–7.20 (m, 24H, ArH); 5.91–5.82 (m, 1H, $CH_2=CH$); 5.26–5.11 (m, 2H, $CH_2=CH$); 3.96 (dt, 2H, $OCH_2CH=CH_2$, ^3J = 6 Hz, ^4J = 1 Hz); 3.81–3.78 (m, 2H, OCH_2CH); 3.73–3.53 (m, 15H, $CH_2O\,CH_2CH_2O\,CH_2CH\,(CH_2)\,OCH_2CH_2OCH_2$); 3.26–3.22 (m, 4H, CH_2OTr). ^{13}C NMR ($CDCl_3$, 25 MHz) δ (ppm): 144.5 (s, Ar); 134.6 (d, $CH_2=CH$); 129.0, 128.0, 127.2 (d, Ar); 117.1 (t, $CH_2=CH$); 86.8 (s, Ar_3C); 78.6 (d, $CHCH_2OAllyl$); 72.6, 71.7, 71.0, 70.6, 63.7 (t, $OCH_2CH_2OCH_2CH_2OTr$ and $CH_2CH(CH_2)OCH_2$). MS (CI) *m/z*: 244 (Tr^+) 100%.

1,14-Di-hydroxy-3,6,9,12-tetroxy-7-allyloxymethyl-tetradecane (12)

A sample of compound **11** (1.19 g, 1.26 mmol) was dissolved in a 1:1 mixture of MeOH/CH_2Cl_2 (10 ml) and 12N HCl (0.85 ml) was added. After stirring at room temperature for 14 h, the solution was cooled to 0°C and neutralized with a saturated aqueous solution of $KHCO_3$. Upon removal of the solvents under reduced pressure and addition of water (30 ml) a white precipitate formed which was filtered off on a Buchner funnel. Water was removed under reduced pressure, the product dissolved in CH_2Cl_2 (30 ml) and the white inorganic salts eliminated. CH_2Cl_2 was distilled off to give pure compound **12**.

Yield: >95%. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 5.89–5.79 (m, 1H, $CH_2=CH$); 5.25–5.10 (m, 2H, $CH_2=CH$); 3.95 (dt, 2H, $OCH_2CH=CH_2$, ^3J = 6 Hz, ^4J = 1.5 Hz); 3.74–3.45 (m, 23H, $OCH_2CH(CH_2O)OCH_2CH_2OCH_2CH_2OH$ and $OCH_2CH_2OCH_2CH_2OH$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 134.5 (d, $CH_2=CH$); 120.0 (t, $CH_2=CH$); 79.5 (d, $CHCH_2OAllyl$); 72.6, 71.5, 70.4, 70.2, 69.8, 69.6, 69.5, (t, $CH_2CH=CH_2$, $HOCH_2CH_2OCH_2CH_2OCH_2CH$ $(CH_2O)OCH_2$ CH_2OH); 62.8 (t, CH_2OH). MS (CI) *m/z*: 308 (M^+) 100%.

1,14-Bis-tosyloxy-3,6,9,12-tetroxy-allyloxymethyl-tetradecane (13)

Compound **13** was obtained as described for ditosylate **7a** using diol **12**. Column chromatography (SiO_2: *n*-hexane : ethyl acetate = 1 : 1).

Yield: 86%. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.77 and 7.76 (2d, 4H, ArH, J = 9 Hz);

7.30 (d, 4H, ArH, J = 9 Hz); 5.91–5.79 (m, 1H, $CH_2=CH$); 5.26–5.10 (m, 2H, $CH_2=CH$); 4.12 (m, 4H, CH_2OSO_2); 3.96 (dt, 2H, $OCH_2CH=CH_2$, $^3J = 6$ Hz, $^4J = 1.5$ Hz); 3.69–3.64 (m, 8H, $CH_2CH_2OCH_2CH_2$); 3.60–3.45 (m, 9H, $CH_2OCH_2CH(CH_2)OCH_2$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 144.7 (s, Ar); 134.7 (s, Ar); 132.8 (d, $CH_2=CH$); 129.7 (d, Ar); 127.7 (d, Ar); 116.5 (t, $CH_2=CH$); 78.2 (d, $CHCH_2OAllyl$); 72.0, 71.1, 70.6, 70.5, 70.4, 69.9, 69.5, 69.3, 68.3 (t, $TsOCH_2CH_2OCH_2CH_2OCH_2CH(CH_2)OCH_2CH_2OCH_2CH_2OTs$); 21.4 (q, CH_3). MS (CI) *m/z*: 617 (MH^+) 20%.

1,3-Di-*iso*-propoxycalix[4]arene-naphtho-crown-6 (2)

To a stirred solution of 1,3-di-*iso*-propoxycalix[4]arene **8** (0.50 g, 1.0 mmol) in dry CH_3CN (350 ml) was added Cs_2CO_3 (1.30 g, 4.0 mmol) and the ditosylate **7a** (0.64 g, 1.0 mmol). The reaction mixture was heated to reflux for 4 days and then the solvent removed under reduced pressure. The residue was extracted in CH_2Cl_2 (50 ml) with 1N HCl (60 ml). The organic phase was washed with 1N HCl (5 × 40 ml) and water (2 × 40 ml). Then the solvent was distilled off and the oily residue was column chromatographied (SiO_2: elution gradient from *n*-hexane: Et_2O 7 : 3 to 2 : 8).

Yield: 95%. M.p.: 182–184°C; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.70 (dd, 2H, J = 6.1 Hz, J = 3.3 Hz, ArH); 7.34 (dd, 2H, J = 6.1 Hz, J = 3.3 Hz, ArH); 7.02 (d, 8H, J = 7.5 Hz, ArH); 6.76 (t, 4H, J = 7.4 Hz, ArH); 6.60 (t, 4H, J = 7.4 Hz, ArH); 4.27 (t, 4H, J = 4.5 Hz, $ArOCH_2$); 4.2–4.13 (m, 4H, $ArOCH_2$); 3.78 (d, 4H, J = 15.4 Hz, $ArCH_2Ar$); 3.73 (d, 4H, J = 15.4 Hz, $ArCH_2Ar$); 3.51 (t, 4H, J = 6 Hz, OCH_2CH_2O); 3.29 (t, 4H, J = 6 Hz, OCH_2CH_2); 0.96 (d, 12H, J = 6 Hz, $OCH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 156.5, 156.8 (s, ArO); 149.3 (s, ArO); 134.8, 133.7 (s, Ar); 130.7, 130.0 (d, Ar); 129.6 (s, Ar); 121.7, 121.6 (d, Ar); 108.9 (d, Ar); 70.8, 70.0, 69.9, 69.7 (t, $OCH_2CH_2OCH_2CH_2$ and $OCH(CH_3)_2$); 38.6 (t, $ArCH_2Ar$); 21.9 (q, $CH(CH_3)_2$). MS (CI) *m/z*: 809 (MH^+) 100%.

1,3-Di-*iso*-propoxycalix[4]arene-binaphtho-crown-6 (3)

Calix-crown **3** was obtained as described above for compound **2** using ditosylate **7b**. The oily residue obtained after extraction was dissolved in hot CH_2Cl_2/MeOH (5 : 1). Upon crystallization, a white solid of pure calix-crown **3** was obtained.

Yield: 90%. M.p.: 272–274°C; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.00 (d, 2H, ArH, J = 9.0 Hz); 7.91 (d, 2H, ArH, J = 9 Hz); 7.57 (d, 2H, ArH, J = 9 Hz); 7.34 (dd, 2H, ArH, J = 6 Hz, J = 3 Hz); 7.22 (dt, 2H, ArH, J = 9 Hz, J = 1.5 Hz); 7.15 (dd, 2H, ArH, J = 6 Hz, J = 1.5 Hz); 7.03 (m, 6H, ArH calix); 6.9 (d, 2H, ArH calix); 6.78 (t, 2H, ArH calix, J = 7.5 Hz); 6.57 (t, 2H, ArH calix, J = 7.5 Hz); 4.16 (m, 4H, $ArOCH_2$); 4.02 (m, 2H, $CH(CH_3)_2$); 3.80 and 3.67 (2d, 2H each, $ArCH_2Ar$, J = 15.3 Hz); 3.79 (s, 4h, $ArCH_2Ar$); 3.45–3.40 (m, 12H, $OCH_2CH_2OCH_2$); 0.90 (s, 12H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 156.5 (s, Ar); 154.7, 154.4 (s, Ar); 134.6, 134.3 (s, Ar); 133.6, 133.4 (s, Ar); 130.2, 129.7, 129.6, 129.4 (d, Ar); 127.9, 126.3, 125.6, 123.7 (d, Ar); 121.9, 121.4 (d, Ar); 120.6, 116.3 (d, Ar); 70.6 (d, $CH(CH_3)_2$); 70.0, 69.2 (t, $CH_2CH_2OCH_2CH_2$); 38.7, 38.6 (t, $ArCH_2Ar$); 21.8 (q, $CH(CH_3)_2$). MS (CI) *m/z*: 935 (M^+) 100%.

1,3-Di-*iso*-propoxycalix[4]arene-7-allyloxymethyl-crown-6 (14)

Calix-crown **14** was obtained as described above for compound **3** using ditosylate **13**. The oily residue obtained after the extraction was column chromatographied (SiO_2: *n*-hexane:ethyl acetate = 1:15).

Yield: 88%. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.07–7.01 (m, 8H, ArH); 6.84–6.77 (m, 4H, ArH); 5.97–5.88 (m, 1H, $CH_2=CH$); 5.33–5.18 (m, 2H, $CH_2=CH$); 4.20 (ept, 2H, $CH(CH_3)_2$,

J = 6 Hz); 4.04 (dt, 2H, $OCH_2CH=CH_2$, $^3J = 6$ Hz, $^4J = 1$ Hz); 3.81 (d, 8H, $ArCH_2Ar$, J = 9 Hz); 3.77–3.23 (m, 21H, $CH_2CH(CH_2)OCH_2CH_2OCH_2CH_2$ and $OCH_2CH_2OCH_2CH_2$); 0.88 (d, 12H, $CH(CH_3)_2$, J = 6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 156.6, 154.8 (s, ArO); 134.7 (d, $CH_2=CH$); 134.5, 133.5 (s, Ar); 130.2, 129.6 (d, Ar); 121.9, 121.6 (d, Ar); 116.9 (t, $CH_2=CH$); 78.6 (d, $CHCH_2OAllyl$); 72.5, 72.3, 71.4, 70.9, 70.2, 69.7, 69.1, 68.9 (t, $OCH_2CH_2OCH_2CH_2O$ calix and $OCH_2CH(CH_2)OCH_2$); 70.4 (d, $OCH(CH_3)_2$); 38.9 (t, $ArCH_2Ar$); 21.7 (q, $CH(CH_3)_2$). MS (CI) *m/z*: 781 (M^+) 100%.

1,3-Di-*iso*-propoxycalix[4]arene-7-hydroxymethyl-crown-6 (15)

A sample of calix-crown **14** (0.56 g, 0.72 mmol) was suspended in 100 ml of a mixture of EtOH/H_2O (1 : 1). To this stirred solution were added a catalytic amount of Pd/C and p-toluene sulfonic acid (PTSA) (0.8 g, 4.21 mmol). After 14h refluxing, the reaction mixture was quenched with water (40 ml) and CH_2Cl_2 (60 ml). This solution was filtered on a Celite bed and the solvent removed from the filtrate under reduced pressure. To the residue was dissolved in CH_2Cl_2 (25 ml) and the organic layer washed with water (2 × 20 ml). Dichloromethane was removed from the organic layer and the product **15** obtained by crystallization from cold MeOH.

Yield: 60%. M.p.: 117°C; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.06–7.01 (m, 8H, ArH); 6.84–6.77 (m, 4H, ArH); 4.23 (ept, 2H, $CH(CH_3)_2$, J = 6 Hz); 3.80 (d, 8H, $ArCH_2Ar$, J = 9 Hz); 3.74–3.28 (m, 21H, $HOCH_2CH(CH_2)OCH_2CH_2OCH_2CH_2$ and $OCH_2CH_2OCH_2CH_2$); 2.3 (s, 1H, OH); 0.89 (d, 12H, $CH(CH_3)_2$, J = 6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 157.7, 154.7 (s, ArO); 134.4, 133.4 (s, Ar); 130.2, 129.6 (d, Ar); 121.9, 121.8, 121.5, 121.4 (d, Ar); 72.5, 71.5, 70.8, 70.7, 70.3, 70.2, 69.8, 69.5, 69.4, 69.2 (t,$OCH_2CH_2OCH_2CH_2OCH_2CH(CH_2)OCH_2$); 70.4 (d, $CH(CH_3)_2$); 62.7 (t, CH_2OH); 38.8 (t, $ArCH_2$ Ar); 21.7 (q, $CH(CH_3)_2$). MS (CI) *m/z*: 740 (M^+) 100%.

1,3-Di-*iso*-propoxycalix[4]arene-7-dansyloxy-crown-6 (4)

To a solution of alcohol **15** (0.08 g, 0.11 mmol) in dry CH_2Cl_2 (50 ml) at 0°C, were added triethylamine (0.03 ml, 0.22 mmol), dansyl chloride (0.03 g, 0.13 mmol) and a catalytic amount of DMAP. After 14h stirring at room temperature, the reaction was quenched adding 0.5N HCl (50 ml). The separated organic phase was washed with water (50 ml) and dichloromethane distilled off. Pure compound **4** was obtained by preparative TLC (SiO_2: Et_2O).

Yield: 50%. M.p.: 120°C. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm) : 8.60 (d, 1H, DNS, J = 8.4 Hz); 8.29 (dd, 2H, DNS, J = 9.3 Hz, J = 1.5 Hz); 7.76–7.75 (m, 2H, DNS); 7.26–7.24 (1H, DNS); 7.02–6.93 (m, 8H, ArH); 6.81–6.66 (m, 4H, ArH); 4.22–4.21 (m, 2H, $CH(CH_3)_2$); 4.18 (d, 2H, CH_2OS, J = 5.6 Hz); 3.80 and 3.78 (2d, 4H each, $ArCH_2Ar$, J = 15.6 Hz); 3.75–3.12 (m, 19H, $ArOCH_2CH_2OCH_2CH_2O$ and OCH_2CH); 2.29 (s, 6H, $N(CH_3)_2$); 0.89 (d, 12H, $CH(CH_3)_2$); J = 6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 156.6, 154.8 (s, Ar ipso); 152.4, 151.8 (s, Ar DNS); 134.5, 133.5 (s, Ar); 131.6, 131.2 (s, Ar DNS); 130.5, 130.3 (d, Ar); 129.9, 129.6, 128.6 (d, Ar DNS); 123.0 (d, Ar DNS); 121.8, 121.6 (d, Ar); 119.5 (d, Ar DNS); 115.5 (d, Ar DNS); 76.9 (d, $CHCH_2O$-DNS); 71.4, 70.8, 70.7, 70.5, 70.0, 69.9, 69.7, 69.5 (t, $OCH_2CH_2OCH_2CH_2O$calix and $CH_2CH(CH_2)OCH_2CH_2$); 70.4 (d, $CH(CH_3)_2$); 38.8 (t, $ArCH_2Ar$); 29.6 (q, $ArN(CH_3)_2$); 21.7 (q, $CH(CH_3)_2$). MS (CI) *m/z*: 974 (MH^+) 100%.

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References

[1] Casnati, A. and Ungaro, R., Calixarenes in Spherical Metal Ion Recognition, In: *Calixarene in Action*; Mandolini, L. and Ungaro, R. Eds., Imperial College Press: London, 2000; pp. 62–84.
[2] Casnati, A., Ungaro, R., Asfari, Z. and Vicens, J., Crown Ethers Derived From Calix[4]arenes; In: *Calix 2001*; Asfari, Z., Böhmer, V., Harrowfield, J. and Vicens, J. Eds., Kluwer Academic Publishers: Dordrecht, 2001, in press.
[3] Casnati, A., Pochini, A., Ungaro, R., Ugozzoli, F., Arnaud, F., Fanni, S., Schwing, M. J., Egberink, R. J. M., de Jong, F. and Reinhoudt, D. N. (1995). *J. Am. Chem. Soc.*, **117**, 2767–2777.
[4] Casnati, A., Pochini, A., Ungaro, R., Bocchi, C., Ugozzoli, F., Egberink, R. J. M., Struijk, H., Lugtenberg, R., de Jong, F. and Reinhoudt, D. N. (1996). *Chem. Eur. J.*, **2**, 436–445.
[5] Chrisstoffels, L. A. J., de Jong, F., Reinhoudt, D. N., Sivelli, S., Gazzola, L., Casnati, A. and Ungaro, R. (1999). *J. Am. Chem. Soc.*, **121**, 10142–10151.
[6] Dozol, J.-F., Lamare, V., Simon, N., Ungaro, R. and Casnati, A., Extraction of Cesium by Calix[4]arene Crown-6: from Synthesis to Process; In: *ACS Symposium Series 757*, Lumetta, G. J., Rogers, R. D. and Gopalan, A. S. Eds., *Am. Chem. Soc.*, Washington, 2000; pp. 12–25.
[7] Lugtenberg, R. J. W., Brzozka, Z., Casnati, A., Ungaro, R., Engbersen, J. F. J. and Reinhoudt, D. N. (1995). *Anal. Chim. Acta*, **310**, 263–267.
[8] Diamond, D. and McKervey, M. A. (1996). *Chem. Soc. Rev.*, **25**, 15–24.
[9] de Silva, P. A., Gunaratne, N. H. Q., Gunnlaugsson, T., Huxley, A. J. M., McCoy, C. P., Rademacher, J. T. and Rice, T. E. (1997). *Chem. Rev.*, **97**, 1515–1566.
[10] Fluorescent Chemosensors for Ion and Molecule Recognition, American Chemical Society: Washington, DC, 1992.
[11] Fabbrizzi, L. and Poggi, A. (1995). *Chem. Soc. Rev.*, **197**, 197–202.
[12] Prodi, L., Bolletta, F., Montalti, M. and Zaccheroni, N. (2000). *Coord. Chem. Rev.*, in press.
[13] Matsumoto, H. and Shinkai, S. (1996). *Tetrahedron Lett.*, **37**, 77–80.
[14] Matsumoto, H. and Shinkai, S. (1994). *Chem. Lett.*, 2431–2434.
[15] Ji, H. F., Brown, G. M. and Dabestani, R. (1999). *Chem. Commun.*, 609–610.
[16] Ji, H. F., Dabestani, R., Hettich, R. L. and Brown, G. M. (1999). *Photochem. Photobiol.*, **70**, 882–886.
[17] Prodi, L., Bolletta, F., Montalti, M., Zaccheroni, N., Casnati, A., Sansone, F. and Ungaro, R., *New J. Chem.*, **24**, 155–158.
[18] Lamare, V., Dozol, J. F., Ugozzoli, F., Casnati, A. and Ungaro, R. (1998). *Eur. J. Org. Chem.*, 1559–1568.
[19] Kim, J. S., Pang, J. H., Yu, I. Y., Lee, W. K., Suh, I. H., Kim, J. K., Cho, M. H., Kim, E. T. and Ra, D. Y. (1999). *J. Chem. Soc., Perkin Trans.*, **2**, 837–846.
[20] Asfari, Z., Bressot, C., Vicens, J., Hill, C., Dozol, J. F., Rouquette, H., Eymard, S., Lamare, V. and Tournois, B. (1995). *Anal. Chem.*, **67**, 3133–3139.
[21] Lamare, V., Dozol, J. F., Fuangswasdi, S., Arnaud-Neu, F., Thuéry, P., Nierlich, M., Asfari, Z. and Vicens, J. (1999). *J. Chem. Soc., Perkin Trans.*, **2**, 271–284.
[22] Kim, J. S., Suh, I. H., Kim, J. K. and Cho, M. H. (1998). *J. Chem. Soc., Perkin Trans.*, **1**, 2307–2311.
[23] Fischer, C., Sarti, G., Casnati, A., Carrettoni, B., Manet, I., Schuurman, R., Guardigli, M., Sabbatini, N. and Ungaro, R. (2000). *Chem. Eur. J.*, **6**, 1026–1034.
[24] Czech, B., Czech, A. and Bartsch, R. A. (1984). *J. Heterocycl. Chem.*, **21**, 341–343.
[25] Reichwein, A. M., Verboom, W. and Reinhoudt, D. N. (1993). *Recl. Trav. Chim. Pays-Bas*, **112**, 358–366.
[26] Verboom, W., Datta, S., Asfari, Z., Harkema, S. and Reinhoudt, D. N. (1992). *J. Org. Chem.*, **57**, 5394–5398.
[27] Casnati, A., de Mendoza, J., Reinhoudt, D. N. and Ungaro, R. (1999). *NATO ASI Ser. C*, **526**, 307–310.
[28] Lein, G. M. and Cram, D. J. (1985). *J. Am. Chem. Soc.*, **107**, 448–455.
[29] Helgeson, R. C., Weisman, G. R., Toner, J. L., Tarnowski, T. L., Chau, L., Mayer, J. M. and Cram, D. J. (1979). *J. Am. Chem. Soc.*, **101**, 4928–4941.
[30] Ungaro, R., El Haj, B. and Smid, J. (1976). *J. Am. Chem. Soc.*, **98**, 5198–5202.
[31] Prodi, L., Bolletta, F., Zaccheroni, N., Watt, C. I. F. and Mooney, N. J. (1998). *Chem. Eur. J.*, **4**, 1090–1094.
[32] Arnaud-Neu, F., Asfari, Z., Souley, B. and Vicens, J. (1996). *New J. Chem.*, **20**, 453–463.
[33] Ballardini, R., Gandolfi, M. T., Prodi, L., Ciano, M., Balzani, V., Köhnke, F., Shariari-Zavariah, H., Spencer, N. and Stoddart, J. F. (1989). *J. Am. Chem. Soc.*, **111**, 7072–7078.
[34] Berlman, I. B., *Handbook of Fluorescence Spectra of Aromatic Compounds*; Academic Press: London, 1995.
[35] Ishow, E., Credi, A., Balzani, V., Spadola, F. and Mandolini, L. (1999). *Chem. Eur. J.*, **3**, 984–989.
[36] Prodi, L., Bolletta, F., Montalti, M. and Zaccheroni, N. (1999). *Eur. J. Inorg. Chem.*, 455–460.
[37] Credi, A. and Prodi, L. (1998). *Spectrochim. Acta*, Part A, **54**, 159–170.
[38] Casnati, A., Comelli, E., Fabbi, M., Bocchi, V., Mori, G., Ugozzoli, F., Manotti Lanfredi, A. M., Pochini, A. and Ungaro, R. (1993). *Recl. Trav. Chim. Pays-Bas*, **112**, 384–392.
[39] Meech, S. R. and Phillips, D. (1983). *J. Photochem.*, **23**, 193–199.
[40] Kyba, E. P., Gokel, G. W., de Jong, F., Koga, K., Sousa, L. R., Siegel, M. G., Kaplan, L., Sogah, G. D. Y. and Cram, D. J. (1977). *J. Org. Chem.*, **42**, 4173–4184.